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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Direct detection of OH formation in the reactions ofHO$_2$ with CH$_3$ C(O)O$_2$ and othersubstituted peroxy radicals" *by* T. J. Dillon and J. N. Crowley

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This paper demonstrates the direct formation of OH radicals in the reactions of HO2 radicals with a variety of peroxy radicals. Production of OH from HO2 + acetyl peroxy has previously been noted in two indirect (product) studies, but it needed a direct method to remove uncertainties surrounding those measurements. The present paper confirms the production of OH in the reaction of HO2 with acetyl peroxy, at a level of 50%, and also shows smaller yields in other peroxy radicals containing alpha- or beta-carbonyl groups, but not beta-hydroxyl groups.

The technique used is pulsed laser photolysis with pulsed LIF detection of OH. Both

HO_2 and the peroxy radicals are produced in the same flash, and the OH, which rapidly gets into steady state, is a spectroscopic marker for the peroxy radical. It is also shown that the overall rate constant for HO_2 + acetyl peroxy is close to the consensus value, even with the addition of a third reaction channel. This fact thus reduces the magnitude of the termination channels which form acetic and peracetic acids.

The paper has some nice subtleties, for example the production of both radicals simultaneously from Cl + ethanol, and the indirect measurement of HO_2 + NO to confirm the HO_2 concentration. The paper can be published with minor changes.

The calibration technique is more complex than I thought initially. The OH signal is calibrated using a small flow of NO, in an excess of HO_2 produced by flash photolysis. As a result of the biexponential kinetics of the OH radical, coupled with its slow production and rapid loss, the peak OH signal is roughly proportional to the NO concentration, but only approaches about 5% of the NO. Thus, although the absolute NO is known, the OH concentration still has to be calculated (or simulated). As such, the technique is subject to some uncertainty, but succeeds, I think, because of the rapid loss rate of OH, which means that other losses of OH can be ignored. The concentrations of the peroxy radicals, on the other hand, are calculated from excimer laser fluence and absorption cross sections, which are themselves subject to uncertainties.

Does it matter that the NO is flowed into the system, while the acetyl peroxy is produced in a smaller volume by the excimer laser. Is there a way to do the experiment so that the NO is also produced by photolysis (e.g. from NO_2)? This would reduce uncertainties in the calculation of laser fluence, and also diffusion effects.

Page 7118, line 17: Does not need nm twice inside the parenthesis.

Page 7119, line 8 (Eq 2) In the font used, the symbols on the top and the bottom look the same! I think one is meant to be laser fluence and the other pathlength, but they are more or less indistinguishable.

Page 7124, line 7. Text (and figure caption) says green triangles; figure shows squares.

Page 7125, line 28. k12 should be k11.

Page 7128, line 25. Replace gg by $>>$.

In Figure 4, is the dip in the OH signal real? It appears that the real yield could be even lower if this represents some kinetically decoupled secondary production.

Page 7129-7130. The discussion of the acetonyl peroxy secondary chemistry is a little confusing. It might be better to repeat the channels (R2a) and (R2b) here, so the reader knows where the CH3CO is coming from.

Reaction (R29a) needs an O2 on the right hand side.

Appendix A R(2a) and R(2b) are the same in the table. (R2a) should form the hydroperoxide

Check the formulas for the radicals formed from isopropyl alcohol. CH3C(OH)CH2 should be CH3CH(OH)CH2, and likewise with the peroxy radicals which follow.

Merge the references for the Appendix with the general references for the final version.

Figure 4 caption, line 3. CH3C(O)O2 should be CH3C(O)CH2O2.

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 7111, 2008.

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